

*The Occurrence of Ozone in the Upper Atmosphere.*

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Part 1.—*Introduction.*

The question of the occurrence of ozone in the atmosphere has been for a long time a subject of much speculation, on account of the important bearing it has, both from physical and chemical considerations, in dealing with many atmospheric phenomena.

Many workers have shown the marked absorption effects that small quantities of ozone have on ultra-violet light.\* The view has also been put forward that this gas plays an important part in contributing to the blue colour of the sky.†

The active chemical properties of ozone would, moreover, if present, be expected to play a very important part in determining the salubrity of the atmosphere, on account of its intense bactericidal action, and its general property of destroying organic matter.

Although a very large amount of work has been done with a view to ascertain the presence and to determine the quantity of ozone in the atmosphere, very few satisfactory attempts have been made to distinguish between this gas and other substances, such as oxides of nitrogen and hydrogen peroxide, which have very similar chemical properties.

The results obtained by different investigators are very discordant, and many of the methods used in extended measurements have since been found quite unreliable, and to give rise to misleading conclusions.

It appears now to be generally accepted that all the forms of test papers

\* Cf. Krüger and Moeller, 'Phys. Zeit.,' vol. 13, p. 729 (1912); Fabry and Buisson, 'Compt. Rend.,' vol. 156, p. 782 (1913).

† *Ut infra.*

and colorimetric methods which have been used so far are not applicable for quantitative results. In some earlier work by the writer, in conjunction with W. Hayhurst,\* a series of measurements on the quantity of ozone in the atmosphere were attempted. By making use of kites and balloons, it was shown that definite small quantities of ozone occur at high altitudes, though no conclusive distinction between this gas, hydrogen peroxide, and oxides of nitrogen was made.

Thierry† had previously made measurements in the Alps at different altitudes. The method used consisted in drawing measured volumes of air through a solution of potassium arsenite, which by reaction with ozone was oxidised to arsenate, and the remaining arsenite was estimated by titrating with a solution of iodine. Some preliminary qualitative tests showed that there was no appreciable quantity of oxides of nitrogen or hydrogen peroxide present to complicate the reaction. Definite quantities of ozone, which increased with the altitude, were found.

H. N. Holmes‡ carried out a series of qualitative tests by exposing papers impregnated with starch and potassium iodide. Definite indications of ozone were found, the amount being greater in winter than in summer.

#### *Part 2.—Some Distinctive Chemical Properties of Ozone.*

A large amount of preliminary work has been done to find some method of determining ozone chemically which would not be vitiated by other gases present in the atmosphere, and which would be simple in application. It was necessary that the method should be capable of use in light apparatus which could be attached to small balloons.

The reagent which was considered most suitable in this application was an aqueous solution of pure potassium iodide. It was found in these preliminary experiments that a concentrated solution reacts with ozone, even when this gas is present at high dilutions, with great rapidity. This is also the case at temperatures as low as  $-50^{\circ}$ , when the gas is passed over the surface of the solid reagent. As the reaction which takes place between ozone and potassium iodide is known to be very complex, it was hoped that an examination of the products obtained would enable a distinction to be made between ozone and other possible reacting gases in the atmosphere.

*Reaction between Potassium Iodide, Ozone, Oxides of Nitrogen, and Hydrogen Peroxide.*—The measurements which were made to ascertain the reactions which take place between these gases and potassium iodide showed that, in

\* 'Chem. Soc. Trans.', vol. 97, p. 868 (1910).

† 'Compt. Rend.', vol. 124, p. 460 (1897).

‡ 'Amer. Chem. Journ.', vol. 47, p. 497 (1912).

the case of ozone, in accordance with an effect of mass action, the nature of the products given by this reaction depends on the total quantity of this gas which has been passed, and also varies in a high degree with the concentration of ozone per unit volume of gas, even when the same total amount of ozone has been passed.\*

It was found that, at a dilution of 1 part in 100,000, the reaction with potassium iodide yields hypo-iodite and free iodine, but no iodate.

The products can be simply estimated by titration with standardised sodium thiosulphate solution, and the absence of iodate ascertained by then acidifying the solution. Any iodate present would cause an immediate liberation of iodine.

Measurements made on the influence of temperature showed that, below  $-24^{\circ}$ , when the reagent was solid, the above relation no longer applied, as, in this case, iodate was formed by ozone at all concentrations.

Oxides of nitrogen were found to react with potassium iodide to give mainly iodate at all concentrations. In this way a basis is provided for the distinction of ozone from nitrogen peroxide when the gases are present at high dilutions, and if the temperature is not below  $-24^{\circ}$ .

Hydrogen peroxide at high dilutions when reacting with potassium iodide gave products similar to those obtained with ozone, so that this reagent does not furnish a distinction between these two gases. However, the difficulty can be overcome by means of a separate test, using titanium sulphate dissolved in sulphuric acid, which gives a yellow coloration in presence of very small quantities of hydrogen peroxide, while ozone produces no effect.

It is seen below that, by the application of these tests to atmospheric measurements at high altitudes, it was established that there was no detectable quantity of hydrogen peroxide or oxides of nitrogen present, but in all cases definite quantities of ozone were found.

### Part 3.—*The Action of Ultra-violet Light on Air.*

The formation of ozone by the action of ultra-violet light on oxygen has been demonstrated by a number of investigators and it has also been shown that this reaction takes place when air is used in place of oxygen.

It has been observed, on the other hand, that ozone is decomposed by ultra-violet light.

Regener† found that an equilibrium stage is obtained when with a certain concentration of ozone no further change is produced on exposing to the light.

\* For further discussion of these reactions, see Pring, 'Chem. News,' vol. 109, p. 73 (1914).

† Regener, 'Ann. d. Phys.,' vol. 20, p. 1033 (1906).

It was found that this equilibrium varies with the temperature and with the nature of the light. Measurements showed that only light of wave-length below  $200 \mu\mu$  is effective in causing the production of ozone from oxygen. This corresponds with the observation of Kreusler that the absorption point of light by oxygen occurs at  $193 \mu\mu$  and below.

It was also found by Regener that the rays which are effective in causing the decomposition of ozone lie between 185 and  $300 \mu\mu$ , which agrees with the measurement made by Meyer, according to which ozone absorbs light of wave-lengths up to  $257 \mu\mu$ . Meyer draws attention to the fact that the solar spectrum ceases at about  $293 \mu\mu$ , and attributes this to the absorption by ozone in the atmosphere.

Von Bahr found that the rate of decomposition of ozone on standing increases rapidly as the pressure is lowered, and thus considers it improbable that any considerable quantity of this gas can exist in the upper atmosphere.

As is recalled below, very little experimental work has been conducted to ascertain the possibility of producing oxides of nitrogen and hydrogen peroxide by ultra-violet radiation.

An investigation was made in this work on the action of ultra-violet light on air, under different conditions of pressure, humidity, etc., in order to obtain some idea of the concentration of ozone that can be reached in this way under the different conditions, and also to see if any other products, such as oxides of nitrogen and hydrogen peroxide, are produced by this action. The apparatus designed for the exposure of the air is shown in fig. 1, and at A, fig. 2.

The main feature in the source of ultra-violet light used consisted in the application of the light, derived from a mercury arc, after passing through a quartz partition, directly to the air undergoing reaction. In this way absorption of the rays by any intervening layer of air was avoided. The quartz tube containing the mercury arc, B, was surrounded with a quartz bulb fitted with the inlet and outlet tubes  $e, e$ , through which the air was circulated. The outside walls of the annular vessel were cooled by submerging the whole apparatus in a vessel of water. The arc was started by means of an induction coil in the following manner. A potential difference of 100 to 200 volts was connected to the terminals  $T_1, T_2$ , after first passing through the lamp resistances joined in series at R (fig. 2). The secondary circuit of the coil made connection with one of these terminals at  $T_1$  and with a wire W, wrapped round the centre of the annular jacket of the lamp. On working the induction coil by means of a tapping key K, a glow discharge was made to pass through the lamp, which started an arc between the reservoirs of mercury at the terminals. When the lamp was immersed in a bath of water, this method of starting was still more

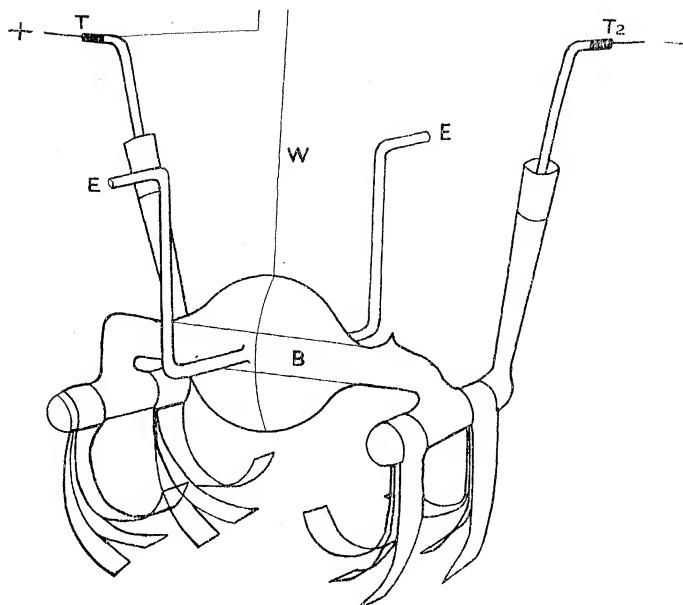


FIG. 1.

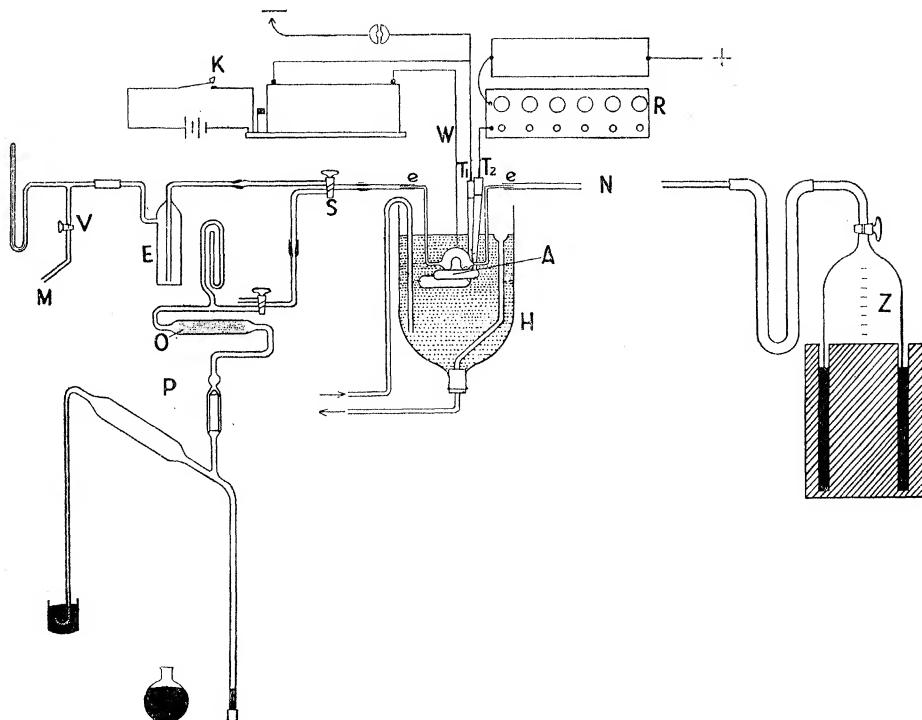


FIG. 2.

effective than when in air, though with the water cooling a higher voltage (200) was necessary to ensure continuous working.

A Töpler pump (P) was connected with the apparatus by means of the two-way tap (S) for the purpose of exhausting and drying. The tube M could be connected with a water pump to aspirate gases at low pressures. The reagent was placed in the wash-bottle E. When estimating ozone, the solution used consisted of equal weights of potassium iodide and water. The water cooling of this apparatus did not of course suffice to maintain a uniform temperature of the contained air.

In addition to this factor of temperature, other conditions prevailing in the upper atmosphere could not be reproduced in these experiments. The nature of the ultra-violet light obtained from the mercury arc was of course limited by the transparency of the quartz, and would thus be expected to differ from the case of solar radiation acting on the uppermost layers of the atmosphere. However, it was possible to obtain conclusive results on the relative formation of ozone, nitrogen peroxide, and hydrogen peroxide, with the particular light used.

*Equilibrium Value of Ozone.*—In measuring the equilibrium value of ozone produced by circulating the air at very low speeds, it was found that the temperature of the lamp quickly imposed a limit to the concentration of ozone. The highest yield of this gas was obtained when the arc was formed intermittently for a very short interval every half minute, thus minimising the rise of temperature. A confined volume of air in the annular space of the lamp was exposed to the radiation. The arc was formed for 1 second every 30 seconds, and the ozone estimated after different intervals in a series of experiments. It was found that the quantity of this gas formed increased rapidly at first and afterwards slowly until, after 40 seconds total exposure, a maximum was practically reached containing 0·15 per cent. ozone.

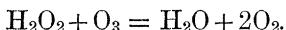
A similar result was obtained when the experiment was conducted with pure dry oxygen, in this case the maximum amount of ozone formed was 0·2 per cent.

E. Regener (*loc. cit.*), when investigating the equilibrium in the production of ozone from oxygen at different temperatures, found this to be 3·4 per cent. at 20°, and 2·7 per cent. at 54°. The discrepancy is probably due to differences in the types of apparatus used, as the equilibrium value would be determined by the relative transparency of the quartz for light of different wave-lengths.

*Influence of Water Vapour on the Formation of Ozone.*—It was found that a more favourable yield in the formation of ozone by ultra-violet

light is obtained with dry air or oxygen than in the case of the moist gas.\*

The smaller yield of ozone in the case of moist air is probably due to the formation of traces of hydrogen peroxide, which reacts with ozone according to the equation



*Effect of Pressure on the Formation of Ozone.*—The apparatus used for this measurement was arranged as shown in fig. 2. The reaction vessel and connecting tubes were exhausted by means of the Töpler pump P, containing phosphorus pentoxide at O.

The air was stored in the gas-holder Z, where it could be dried by leaving in contact with phosphorus pentoxide for several days. By means of the tap S, which was lubricated with phosphoric acid, the gas, after passing through the radiation vessel, could be led through the reagent placed in the wash-bottle E. In the comparative experiments 200 c.c. of air was passed in equal intervals of time, but at pressures varying from 760 to 30 mm.

It was found that a marked fall in the ozone formation occurred with reduction of pressure. Thus, at 760 mm., the concentration reached was 0·01 per cent., and at 30 mm. 0·0014 per cent.

*Formation of Hydrogen Peroxide.*—The action of ultra-violet radiation on water has been investigated by Kernbaum,† who found that a slight decomposition slowly takes place according to the equation



Chlopin‡ investigated the formation of hydrogen peroxide from moist air when submitted to the radiation from a mercury arc lamp constructed of quartz. The air was circulated through the reaction vessel at a speed of 35 litres per hour, and then passed through a solution of titanic acid dissolved in dilute sulphuric acid. After passing the gas for 10 minutes this reagent assumed a slight yellow colour, indicating the presence of traces of hydrogen peroxide.

In the present work experiments were made to detect the formation of hydrogen peroxide by passing 60 litres of moist air through the apparatus during two hours, and leading through a solution of titanic acid in sulphuric acid and contained in a small glass spiral washer. No change in colour was observed. A comparative test made by taking hydrogen

\* Cf. Warburg and Leithäuser, 'Ann. d. Phys.', vol. 20, p. 751 (1906).

† 'Le Radium,' vol. 6, p. 225 (1909).

‡ 'Zeit. anorg. Chem.', vol. 71, p. 198 (1911).

peroxide solution showed that it is possible to detect with certainty the presence of  $0.1 \times 10^{-6}$  grm. equivalent of this compound with the above reagent. In 60 litres of air this would correspond to a volume of  $1.8 \times 10^{-6}$  per cent. The amount formed under the conditions of the above experiment must therefore be below this value, which is very small compared with the ozone.

As hydrogen peroxide is decomposed by ozone, it is doubtful whether any appreciable quantity would be permanently stable in presence of the latter gas.

*Formation of Oxides of Nitrogen.*—It has not yet been established whether oxides of nitrogen are formed by ultra-violet light, though Chlopin (*loc. cit.*) obtained evidence of the formation of traces of this gas by applying metaphenylenediamine as a colorimetric test. This method is extremely sensitive and open to doubt when applied in this connection. In the present work, use was made of a method devised by Fischer and Marx\* for distinguishing nitrogen peroxide from ozone, which depends on the fact that, when a mixture of the gases is passed into liquid air, the former separates as a white solid while the latter dissolves. Measurements were made in the present case with purified air which was circulated through the radiation apparatus during intervals of several hours, and then passed into liquid air. After filtering off the solid particles, these were allowed to evaporate and pass into a gas-holder. No nitrogen peroxide could be detected in this gas by applying potassium iodide or tetramethyl base paper. These results show that, as in the case of hydrogen peroxide, if any nitrogen peroxide is produced by ultra-violet light, as used in these experiments, the quantity is negligibly small when compared with the ozone.

#### Part 4.—*Atmospheric Measurements at High Altitudes.*

A. *In the Alps, at Altitudes between 2000 and 3500 metres.*—The absorbing vessel which was used to contain the reagent was the same as that employed in the earlier work of Hayhurst and Pring (*loc. cit.*), and consisted of a spherical glass bulb of 5 cm. diameter (B, fig. 3), which was provided with an inlet and outlet tube 1 cm. internal diameter terminating in conical funnels (C, C) on the outside, and projecting, on the inside, for some distance inside the bulb. In this way a quantity of reagent could be placed inside the bulb and secured against loss when the apparatus was placed in any position. A free circulation of air through the vessel took place, when this was placed horizontally and exposed to a wind. The glass

\* 'Ber.,' vol. 39, p. 2557 (1906).

funnels C, C, were extended by means of paper (D, D), and the whole enclosed in a cage of hard spring wire (BB) for protection. The glass vessel was blackened on the outside and also covered with black cloth to protect the reagent from light.

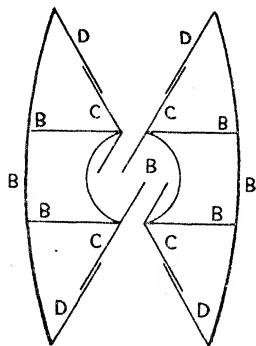


FIG. 3.

By placing a fuming liquid in the vessel and exposing to a wind, the air in passing through was seen to assume a rapid circulatory motion inside. The efficiency of the absorption of ozone during this passage was tested by taking a vessel of similar construction, placing the potassium iodide reagent inside, and then joining the vessel in series with a wash-bottle containing the same reagent. On passing ozonised air through the two vessels in succession, and varying the speed of circulation, it

was found that even at higher velocities than those subsequently given by the atmosphere, more than four-fifths of the ozone was in every case absorbed by the first vessel.

*Volume of Air Circulated through the Reaction Vessel during a Measurement.*—An approximate calibration of the volume of air circulated, which was assumed to be directly proportional to the velocity of the wind, was made by placing some pure benzene in the vessel, and after exposing for definite intervals to a wind of known velocity, noticing the loss in weight.

The vessel was first calibrated in terms of the readings given by a portable anemometer kindly lent by the Meteorological Office, and then by comparison with a standardised anemometer at the Manchester University Observatory; the readings were reduced to miles per hour.

#### Results of Calibration.

	Temperature of benzene.	Units, anemo-meter scale.	Loss of weight of benzene.	Loss of weight per unit of anemo-meter scale.
Vessel 1 .....	18·0°	135	grm. 5·30	grm. 0·0392
" 1 .....	18·0	95	4·70	0·0495
" 1 .....	16·5	70	2·67	0·0382
" 2 .....	17·0	81	3·55	0·0440
" 2 .....	17·0	97	4·35	0·0449
Mean .....	17·0	—	—	0·0433

Since the vapour pressure of benzene at 17° is 66·5 mm. and its molecular weight 78, it follows that 1 grm. of the saturated vapour will occupy

3.29 litres. The quantity displaced during a reading of 1 unit on the anemometer, viz., 0.043 grm., will therefore correspond to 0.141 litre.

The calibration of the anemometer showed that 1 unit corresponded to a horizontal flow of air of 0.027 mile, so that a flow of wind corresponding to a displacement past the apparatus of 1 mile corresponds to a circulation of 5.12 litres in the vessel.

*Results of Measurements made in the Alps.*—The tests, which lasted several days, were made near Scheidegg at an altitude of 2130 metres and at a point near the Jungfraujoch of 3580 metres altitude.

*Hydrogen Peroxide.*—This was tested for by exposing titanic acid in presence of sulphuric acid to the wind in an apparatus similar to that used for the ozone estimation. The colour of this reagent remained quite unchanged after exposing for two days at the different altitudes and under different conditions of weather, thus showing that there is no appreciable quantity of hydrogen peroxide in the atmosphere. It was noticed, however, that freshly fallen snow or hail gave a very marked coloration with the reagent. No tests were made with glacier water, though this would be expected to retain the hydrogen peroxide associated with the snow.

*Nitrogen Peroxide.*—In the experiments tabulated below, where estimations have been made of ozone, it was found that in no case was any potassium iodate formed on exposing the iodide in the reaction vessel to the atmosphere.

Time of measurement.	Altitude.	Units, anemo- meter.	Litres of air circulated.	Total volume of ozone (at N.T.P.).	Volume of ozone per unit volume of air.
Aug. 22-23, 1913— 7.0 P.M. to 8.0 A.M. ....	metres. 2130	110	15.2	c.c. 0.05	0.000003
Aug. 23— 8.0 A.M. to 7.0 P.M. ....	2130	813	113	0.31	0.0000027
Aug. 23-24— 7.0 P.M. to 8.0 A.M. ....	2130	3176	438	0.87	0.00000197
Mean value at 6970 feet (2130 metres).....					$2.5 \times 10^{-6}$
Aug. 24— 6.0 to 7.30 P.M. ....	3580	1195	165	0.62	0.0000038
Aug. 25— 8.50 A.M. to 5.45 P.M. ....	3580	10694	1470	7.1	0.0000048
Aug. 26— 6.0 A.M. to 6.0 P.M. ....	3580	1520	210	1.18	0.0000056
Mean value at 11690 feet (3580 metres) .....					$4.7 \times 10^{-6}$

As pointed out above this shows the absence of any appreciable quantity of oxides of nitrogen.

*Ozone Estimations.*—These were made by placing about 7 c.c. of a mixture of equal weights of potassium iodide and water in the reaction vessel and placing on the ground horizontally in the direction of the wind. The anemometer was erected in the neighbourhood.

The mean quantity of ozone, viz.,  $2\cdot5 \times 10^{-6}$  at 2130 metres and  $4\cdot7 \times 10^{-6}$  at 3580 metres, are in close agreement with the results obtained by de Thierry (*loc. cit.*), which gave  $1\cdot6 \times 10^{-6}$  at 1050 metres and  $4\cdot4 \times 10^{-6}$  at 3020 metres.

B. *Measurements made with Free Balloons.*—For these measurements use was made of the hydrogen balloons which are used in meteorological investigations at the Manchester University. These balloons with the attached instruments rise to an average height of about 10 miles and then burst. The deflated skin retards the rate of fall of the instruments to the ground. A knowledge of the height attained and the temperature is obtained by a recording baro- and thermograph.

The reaction vessel for the ozone tests was of the same form as that used in the tests at ground level, and was suspended vertically from the balloon together with the other instruments.

A rough calculation of the amount of air which would pass through the vessel during an ascent and descent was made from the following data:—

From the calibration made above it was seen that the exposure of the vessel to a flow of wind corresponding to a displacement of air of 1 mile caused the passage of 5·12 litres. Since 1 mile =  $1\cdot6 \times 10^5$  cm., it follows that a displacement of 1 cm. at atmospheric pressure will cause the circulation of  $(5\cdot12 \times 10^3)/(1\cdot6 \times 10^5) = 0\cdot032$  c.c.

On the assumption that the volume circulated is proportional to the displacement through the air, it follows that during an ascent and descent the mass of air passed through in grammes is given by  $2(p_1 - p_2) \times 13\cdot6 \times 0\cdot032$ , or  $0\cdot87(p_1 - p_2)$ , where  $p_1$  is the atmospheric pressure in centimetres of mercury at ground level,  $p_2$  that at the highest level reached, and 13·6 the density of mercury. The volume circulated in litres (measured at N.T.P.) is therefore  $0\cdot675(p_1 - p_2)$ .

The values for the pressure at different altitudes have been taken from meteorological tables, as reproduced on p. 215.

At a height of about 6000 metres the temperature is always below the freezing point of the reagent ( $-24^\circ$ ) so that reaction must take place with the solid. It was seen in Part 1 that under these conditions the method applied did not enable a distinction between ozone and oxides of

nitrogen. However, in all measurements made up to 6500 metres, the latter gas was found not to be present in any appreciable quantity.

Altitude.	Pressure.	Altitude.	Pressure.	Altitude.	Pressure.
metres.	mm.	metres.	mm.	metres.	mm.
1000	673	4000	458	8000	267
1500	631	5000	401	9000	233
2000	586	6000	353	11000	168
3000	522	7000	308	20000	39

The reagent placed in the vessel consisted of 5 to 7 c.c. of the 50-percent. potassium iodide solution as used in all the other measurements. After being returned by the finder through the post the amount of solution remaining usually amounted to about 2 c.c. The values given in the tables are calculated on the original quantity of reagent.

Time of ascent.	Mean direction of wind.	Height attained.	Estimated volume of air circulated.	Weight of iodine liberated in total reagent.		Potassium hydrate formed.	Mean concentration of ozone in 1 volume air.
				Free I <sub>2</sub> (+ hypo-iodite).	Combined I <sub>2</sub> (as iodate, etc.).		
Aug. 3, 1909— 9.0 P.M. ....	W.S.W.	kilom. 16·0	litres. 46·6	mgm.	mgm.	mgm.	$4 \cdot 8 \times 10^{-7}$
March 18, 1910— 12.0 NIGHT.....		N.	13·5	0·12	0·13	0·004	$6 \cdot 8 \times 10^{-7}$
9 P.M. ....	N.	8·5	34·7	1·02	0·70	Nil	$4 \cdot 4 \times 10^{-6}$
March 19— 2.0 A.M. ....	N.	19·5	48·1	0·40	1·12		$2 \cdot 8 \times 10^{-6}$
May 18— 9.40 P.M. ....	S.	17·0	47·5	0·76	0·76		$2 \cdot 8 \times 10^{-6}$
May 19— 2.10 A.M. ....	S.	12·0	43·8	0·13	0·34	trace	$9 \cdot 5 \times 10^{-7}$
6.30 A.M. ....	S.	20·0	48·3	0·21	0·40		$1 \cdot 1 \times 10^{-6}$
March 1, 1911— 5.30 P.M. ....	N.W.	19·0	48·2	0·303	0·682	Nil	$1 \cdot 8 \times 10^{-6}$
May 4— 7.15 P.M. ....	N.W.	20·0	48·3	0·612	2·36	Nil	$5 \cdot 4 \times 10^{-6}$
Aug. 6, 1913— 8.0 P.M. ....	N.N.E.	6·5	29·8	0·416	Nil		$1 \cdot 2 \times 10^{-6}$
Mean.....							$2 \cdot 1 \times 10^{-6}$

It is seen that, except in one case, a large part of the reaction had resulted in the formation of iodate. The one case in which this compound had not formed was where the ascent had only reached an altitude of 6·5 kilometres, where the temperature indicated was  $-31\cdot5^{\circ}$ . Since the cryoscopic point of the reagent is  $-24^{\circ}$ , complete solidification had probably not occurred.

The fact that, as in the case of all measurements at lower altitudes, there was no iodate formed in this experiment, indicated the absence of oxides of nitrogen, and the formation of iodate in experiments at greater altitudes is presumably due to the reaction of ozone on the solid reagent, as was established in laboratory experiments.

By considering these results together with those made on ground level at altitudes up to 3·5 kilometres, the conclusion may be drawn that there is no detectable amount of hydrogen peroxide or oxides of nitrogen in the higher atmosphere, but that there is a definite small quantity of ozone. The amount of this last gas increases with the altitude up to 3·5 kilometres.

The mean values estimated in the measurements made in the Alps were  $2\cdot5 \times 10^{-6}$  in one part of air at 2·5 kilometres altitude, and  $4\cdot7 \times 10^{-6}$  parts at 3·5 kilometres.

In the measurements made with the balloons in this country, the mean volume of ozone between ground level and altitudes up to 20 kilometres gave an average value of  $2\cdot1 \times 10^{-6}$ . Even after allowing for the absence of this gas at lower levels on account of organic impurities, this value would indicate that there is no very great increase in the amount of ozone in the atmosphere between altitudes of 4 and 20 kilometres. The amounts measured, however, are known to be sufficient to exhibit marked absorption and chemical effects, and thus play an important part in the permeability to radiation and in the chemical purification of the atmosphere.

#### *Part 5.—The Part played by Ozone in Determining the Blue Colour of the Sky.*

The blue colour of the sky has been ascribed to a number of operating causes. Firstly, the turbidity of the air or presence of small particles of dust has been shown to exert a selective reflection on light of different wavelengths.

Secondly, it has been pointed out that the molecules of the air are themselves able to scatter radiation in a similar manner to the action of small particles of dust.\*

Thirdly, the presence of ozone has been put forward by a number of investigators to account for this colour.†

The coloration has also been attributed to fluorescence phenomena produced by this gas.‡

\* Cf. Rayleigh, 'Phil. Mag.', vol. 47, p. 375 (1899); Schuster, 'Theory of Optics,' p. 328 (1909); 'Nature,' vol. 81, p. 97 (1909); King, 'Phil. Trans.,' A, vol. 212, p. 375 (1913).

† Cf. Chappuis, 'Comptes Rendus,' vol. 91, p. 985 (1880); Hartley, 'Chem. Soc. Trans.,' vol. 39, p. 111 (1881); Spring, 'Bull. de l'Acad. Belge' (3), vol. 36, p. 504.

‡ Cf. Lallemand, 'Comptes Rendus,' vol. 75, p. 707 (1872); Hartley, 'Nature,' vol. 39, p. 474 (1889).

It has been found\* from spectrophotometric measurements on skylight that the distribution of intensity observed could not be altogether accounted for by the assumption of an atmosphere conforming to Rayleigh's formula nor of a turbid medium containing coarser particles. These, and the results of other investigators, indicate that there is a blue absorption colour of the air.

In the present work the results of the approximate measurements made on the quantity of ozone in the atmosphere at altitudes ranging up to 20 kilometres supply data which enabled a rough comparison to be made in the laboratory of the depth of colour given by ozone of equivalent amount.

For this experiment a glass tube of 2·8 metres length and 4 cm. diameter was taken. The walls were provided with side tubes, one near each end, to enable the passage of the ozonised gas through the tube. The two ends of the main tube were covered by thin plates of glass, which were cemented by sodium silicate solution so as to make air-tight connection.

The outside of the tube was wrapped with black paper, and a white paper disc placed over one of the end plates. On illuminating this by daylight and sighting through the other end, the intensity of coloration produced on admitting ozone of known concentration could be observed.

The ozone for this purpose was prepared from oxygen by passing through a number of annular glass tubes where it was exposed to the silent electric discharge produced by an induction coil. After time had been allowed for the composition of the gas in the sighting tube to become uniform, an analysis of the gas was made by connecting the outlet side tube to a vessel containing acidified potassium iodide solution, and allowing a known volume of the gas to pass.

It is seen from the atmospheric measurements that, in this country, an approximate concentration of two parts of ozone in one million of air was found as the average amount of this gas between ground level and an altitude of 20 kilometres, while the amount found in the Alps at an altitude of 3½ kilometres was five parts in one million. Taking this second value, and allowing 8360 metres as the height which would be occupied by the atmosphere if at N.T.P., this concentration of ozone in a vertical section of the atmosphere is equivalent to a layer of the pure gas of a thickness of 4·2 cm. (at N.T.P.).

The results given in the tables below record the observations made with the sighting tube when filled with oxygen containing different concentrations of ozone. The thickness of the layer of pure gas which is equivalent to this concentration is also given.

\* Nichols, 'Phys. Review,' vol. 26, p. 497 (1908).

Percentage concentration of ozone in oxygen.	Equivalent thickness of layer of pure ozone. cm.	Colour observed.
0·20	0·55	Colour uncertain.
0·36	1·0	Faint bluish-green.
1·7	4·7	Marked blue colour.
2·8	7·8	Deep steel blue colour.

It is difficult to compare the colour of the gas in a tube of this nature with that of the sky on account of a large influence exerted by the nature of the illumination.

The results obtained, however, indicate that the presence of ozone is a contributing factor to the blue colour.

This work is being extended with a view to determining more precisely the quantity of ozone in the upper atmosphere, its variation from time to time and with altitude, and its influence on the constant of solar radiation.

#### *Summary.*

A method has been devised which enables an estimation to be made of ozone when at very high dilutions, and at temperatures down to  $-60^{\circ}$ . With very dilute gases, the reagent used, consisting of an aqueous solution of potassium iodide, enables a distinction to be made between ozone and oxides of nitrogen, if the temperature is not below the freezing point of the reagent ( $-24^{\circ}$ ).

By applying a source of light given by a mercury arc in a quartz vessel it was found that ozone is formed up to a certain equilibrium stage. The rate of formation of the gas is only slightly lowered by the presence of water vapour, but decreases rapidly with falling pressure.

By exposing air to the source of light used, no formation of oxides of nitrogen or hydrogen peroxide could be detected. Estimations made of the quantity of ozone in the atmosphere at high altitudes in this country showed an average amount of  $2\cdot5 \times 10^{-6}$  in one volume of air, and that no very large increase occurs between 5 kilometres and the highest altitude reached, viz. 20 kilometres. In the Alps, a mean value of  $2\cdot5 \times 10^{-6}$  was measured at an altitude of 2100 metres, and  $4\cdot7 \times 10^{-6}$  at 3580 metres. No detectable amounts of oxides of nitrogen or hydrogen peroxide were found in either of the last two cases. It was found by colorimetric measurements in the laboratory that this last amount of ozone gives a marked blue colour, thus showing that ozone must be regarded as a contributing factor in determining the blue colour of the sky.

In conclusion I wish to express my thanks to Sir Ernest Rutherford for the kind interest he has taken in this work, to Miss M. White for the loan of meteorological balloons, and to the Director of the Jungfrau Railway for travelling facilities he generously extended.

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*On the Diffraction of Light by Spheres of Small Relative Index.*

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In a short paper "On the Diffraction of Light by Particles Comparable with the Wave-length,"\* Keen and Porter describe curious observations upon the intensity and colour of the light transmitted through small particles of precipitated sulphur, while still in a state of suspension, when the size of the particles is comparable with, or decidedly larger than, the wave-length of the light. The particles principally concerned in their experiments appear to have decidedly exceeded those dealt with in a recent paper,† where the calculations were pushed only to the point where the circumference of the sphere is  $2\cdot25 \lambda$ . The authors cited give as the size of the particles, when the intensity of the light passing through was a minimum,  $6$  to  $10 \mu$ , that is over 10 wave-lengths of yellow light, and they point out the desirability of extending the theory to larger spheres.

The calculations referred to related to the particular case where the (relative) refractive index of the spherical obstacles is 1·5. This value was chosen in order to bring out the peculiar polarisation phenomena observed in the diffracted light at angles in the neighbourhood of  $90^\circ$ , and as not inappropriate to experiments upon particles of high index suspended in water. I remarked that the extension of the calculations to greater particles would be of interest, but that the arithmetical work would rapidly become heavy.

There is, however, another particular case of a more tractable character, viz., when the relative refractive index is *small*; and although it may not be

\* 'Roy. Soc. Proc.,' A, vol. 89, p. 370 (1913).

† 'Roy. Soc. Proc.,' A, vol. 84, p. 25 (1910); 'Scientific Papers,' vol. 5, p. 547.